

Chapter 6

Design for Single Reactions

There are many ways of processing a fluid: in a single batch or flow reactor, in a chain of reactors possibly with interstage feed injection or heating, in a reactor with recycle of the product stream using various feed ratios and conditions, and so on. Which scheme should we use? Unfortunately, numerous factors may have to be considered in answering this question; for example, the reaction type, planned scale of production, cost of equipment and operations, safety, stability and flexibility of operation, equipment life expectancy, length of time that the product is expected to be manufactured, ease of convertibility of the equipment to modified operating conditions or to new and different processes. With the wide choice of systems available and with the many factors to be considered, no neat formula can be expected to give the optimum setup. Experience, engineering judgment, and a sound knowledge of the characteristics of the various reactor systems are all needed in selecting a reasonably good design and, needless to say, the choice in the last analysis will be dictated by the economics of the overall process.

The reactor system selected will influence the economics of the process by dictating the size of the units needed and by fixing the ratio of products formed. The first factor, reactor size, may well vary a hundredfold among competing designs while the second factor, product distribution, is usually of prime consideration where it can be varied and controlled.

In this chapter we deal with *single reactions*. These are reactions whose progress can be described and followed adequately by using one and only one rate expression coupled with the necessary stoichiometric and equilibrium expressions. For such reactions product distribution is fixed; hence, the important factor in comparing designs is the reactor size. We consider in turn the size comparison of various single and multiple ideal reactor systems. Then we introduce the recycle reactor and develop its performance equations. Finally, we treat a rather unique type of reaction, the autocatalytic reaction, and show how to apply our findings to it.

Design for multiple reactions, for which the primary consideration is product distribution, is treated in the next two chapters.

6.1 SIZE COMPARISON OF SINGLE REACTORS

Batch Reactor

First of all, before we compare flow reactors, let us mention the batch reactor briefly. The batch reactor has the advantage of small instrumentation cost and flexibility of operation (may be shut down easily and quickly). It has the disadvantage of high labor and handling cost, often considerable shutdown time to empty, clean out, and refill, and poorer quality control of the product. Hence we may generalize to state that the batch reactor is well suited to produce small amounts of material and to produce many different products from one piece of equipment. On the other hand, for the chemical treatment of materials in large amounts the continuous process is nearly always found to be more economical.

Regarding reactor sizes, a comparison of Eqs. 5.4 and 5.19 for a given duty and for $\varepsilon = 0$ shows that an element of fluid reacts for the same length of time in the batch and in the plug flow reactor. Thus, the same volume of these reactors is needed to do a given job. Of course, on a long-term production basis we must correct the size requirement estimate to account for the shutdown time between batches. Still, it is easy to relate the performance capabilities of the batch reactor with the plug flow reactor.

Mixed Versus Plug Flow Reactors, First- and Second-Order Reactions

For a given duty the ratio of sizes of mixed and plug flow reactors will depend on the extent of reaction, the stoichiometry, and the form of the rate equation. For the general case, a comparison of Eqs. 5.11 and 5.17 will give this size ratio. Let us make this comparison for the large class of reactions approximated by the simple n th-order rate law

$$-r_A = -\frac{1}{V} \frac{dN_A}{dt} = kC_A^n$$

where n varies anywhere from zero to three. For mixed flow Eq. 5.11 gives

$$\tau_m = \left(\frac{C_{A0}V}{F_{A0}} \right)_m = \frac{C_{A0}X_A}{-r_A} = \frac{1}{kC_{A0}^{n-1}} \frac{X_A(1 + \varepsilon_A X_A)^n}{(1 - X_A)^n}$$

whereas for plug flow Eq. 5.17 gives

$$\tau_p = \left(\frac{C_{A0}V}{F_{A0}} \right)_p = C_{A0} \int_0^{X_A} \frac{dX_A}{-r_A} = \frac{1}{kC_{A0}^{n-1}} \int_0^{X_A} \frac{(1 + \varepsilon_A X_A)^n dX_A}{(1 - X_A)^n}$$

Dividing we find that

$$\frac{(\tau C_{A0}^{n-1})_m}{(\tau C_{A0}^{n-1})_p} = \frac{\left(\frac{C_{A0}^n V}{F_{A0}} \right)_m}{\left(\frac{C_{A0}^n V}{F_{A0}} \right)_p} = \frac{\left[X_A \left(\frac{1 + \varepsilon_A X_A}{1 - X_A} \right)^n \right]_m}{\left[\int_0^{X_A} \left(\frac{1 + \varepsilon_A X_A}{1 - X_A} \right)^n dX_A \right]_p} \quad (1)$$

With constant density, or $\varepsilon = 0$, this expression integrates to

$$\frac{(\tau C_{A0}^{n-1})_m}{(\tau C_{A0}^{n-1})_p} = \frac{\left[\frac{X_A}{(1 - X_A)^n} \right]_m}{\left[\frac{(1 - X_A)^{1-n} - 1}{n - 1} \right]_p}, \quad n \neq 1$$

or

$$\frac{(\tau C_{A0}^{n-1})_m}{(\tau C_{A0}^{n-1})_p} = \frac{\left(\frac{X_A}{1 - X_A} \right)_m}{-\ln(1 - X_A)_p}, \quad n = 1$$

(2)

Equations 1 and 2 are displayed in graphical form in Fig. 6.1 to provide a quick comparison of the performance of plug flow with mixed flow reactors. For

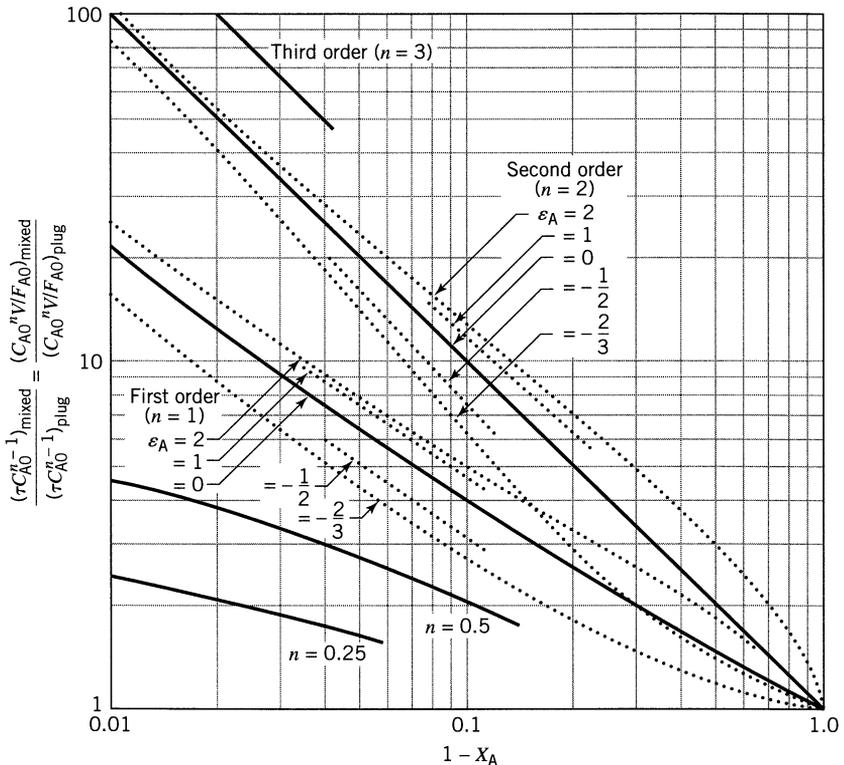


Figure 6.1 Comparison of performance of single mixed flow and plug flow reactors for the n th-order reactions



The ordinate becomes the volume ratio V_m/V_p or space-time ratio τ_m/τ_p if the same quantities of identical feed are used.

identical feed composition C_{A0} and flow rate F_{A0} the ordinate of this figure gives directly the volume ratio required for any specified conversion. Figure 6.1 shows the following.

1. For any particular duty and for all positive reaction orders the mixed reactor is always larger than the plug flow reactor. The ratio of volumes increases with reaction order.
2. When conversion is small, the reactor performance is only slightly affected by flow type. The performance ratio increases very rapidly at high conversion; consequently, a proper representation of the flow becomes very important in this range of conversion.
3. Density variation during reaction affects design; however, it is normally of secondary importance compared to the difference in flow type.

Figures 6.5 and 6.6 show the same first- and second-order curves for $\varepsilon = 0$ but also include dashed lines which represent fixed values of the dimensionless reaction rate group, defined as

$k\tau$ for first-order reaction

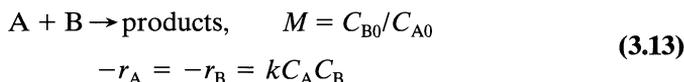
$kC_{A0}\tau$ for second-order reaction

With these lines we can compare different reactor types, reactor sizes, and conversion levels.

Example 6.1 illustrates the use of these charts.

Variation of Reactant Ratio for Second-Order Reactions

Second-order reactions of two components and of the type



behave as second-order reactions of one component when the reactant ratio is unity. Thus

$$-r_A = kC_A C_B = kC_A^2 \quad \text{when } M = 1 \quad (3)$$

On the other hand, when a large excess of reactant B is used then its concentration does not change appreciably ($C_B \cong C_{B0}$) and the reaction approaches first-order behavior with respect to the limiting component A, or

$$-r_A = kC_A C_B = (kC_{B0})C_A = k'C_A \quad \text{when } M \gg 1 \quad (4)$$

Thus in Fig. 6.1, and in terms of the limiting component A, the size ratio of mixed to plug flow reactors is represented by the region between the first-order and the second-order curves.

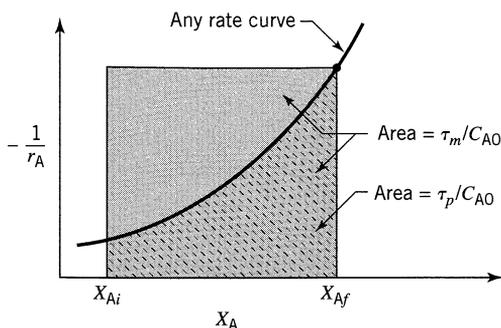


Figure 6.2 Comparison of performance of mixed flow and plug flow reactors for any reaction kinetics.

General Graphical Comparison

For reactions with arbitrary but known rate the performance capabilities of mixed and plug flow reactors are best illustrated in Fig. 6.2. The ratio of shaded and of hatched areas gives the ratio of space-times needed in these two reactors.

The rate curve drawn in Fig. 6.2 is typical of the large class of reactions whose rate decreases continually on approach to equilibrium (this includes all n th-order reactions, $n > 0$). For such reactions it can be seen that mixed flow always needs a larger volume than does plug flow for any given duty.

6.2 MULTIPLE-REACTOR SYSTEMS

Plug Flow Reactors in Series and/or in Parallel

Consider N plug flow reactors connected in series, and let X_1, X_2, \dots, X_N be the fractional conversion of component A leaving reactor 1, 2, \dots , N . Basing the material balance on the feed rate of A to the first reactor, we find for the i th reactor from Eq. 5.18

$$\frac{V_i}{F_0} = \int_{X_{i-1}}^{X_i} \frac{dX}{-r}$$

or for the N reactors in series

$$\begin{aligned} \frac{V}{F_0} &= \sum_{i=1}^N \frac{V_i}{F_0} = \frac{V_1 + V_2 + \dots + V_N}{F_0} \\ &= \int_{X_0=0}^{X_1} \frac{dX}{-r} + \int_{X_1}^{X_2} \frac{dX}{-r} + \dots + \int_{X_{N-1}}^{X_N} \frac{dX}{-r} = \int_0^{X_N} \frac{dX}{-r} \end{aligned}$$

Hence, N plug flow reactors in series with a total volume V gives the same conversion as a single plug flow reactor of volume V .

For the optimum hook up of plug flow reactors connected in parallel or in any parallel-series combination, we can treat the whole system as a single plug flow reactor of volume equal to the total volume of the individual units if the feed is distributed in such a manner that fluid streams that meet have the same composition. Thus, for reactors in parallel V/F or τ must be the same for each parallel line. Any other way of feeding is less efficient.

EXAMPLE 6.1 OPERATING A NUMBER OF PLUG FLOW REACTORS

The reactor setup shown in Fig. E6.1 consists of three plug flow reactors in two parallel branches. Branch D has a reactor of volume 50 liters followed by a reactor of volume 30 liters. Branch E has a reactor of volume 40 liters. What fraction of the feed should go to branch D?

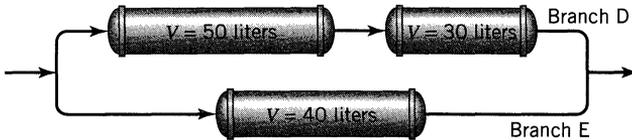


Figure E6.1

SOLUTION

Branch D consists of two reactors in series; hence, it may be considered to be a single reactor of volume

$$V_D = 50 + 30 = 80 \text{ liters}$$

Now for reactors in parallel V/F must be identical if the conversion is to be the same in each branch. Therefore,

$$\left(\frac{V}{F}\right)_D = \left(\frac{V}{F}\right)_E$$

or

$$\frac{F_D}{F_E} = \frac{V_D}{V_E} = \frac{80}{40} = 2$$

Therefore, two-thirds of the feed must be fed to branch D.

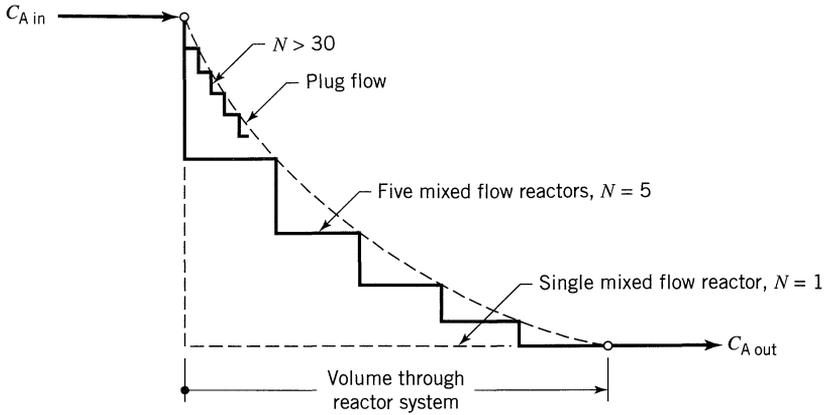


Figure 6.3 Concentration profile through an N -stage mixed flow reactor system compared with single flow reactors.

Equal-Size Mixed Flow Reactors in Series

In plug flow, the concentration of reactant decreases progressively through the system; in mixed flow, the concentration drops immediately to a low value. Because of this fact, a plug flow reactor is more efficient than a mixed flow reactor for reactions whose rates increase with reactant concentration, such as n th-order irreversible reactions, $n > 0$.

Consider a system of N mixed flow reactors connected in series. Though the concentration is uniform in each reactor, there is, nevertheless, a change in concentration as fluid moves from reactor to reactor. This stepwise drop in concentration, illustrated in Fig. 6.3, suggests that the larger the number of units in series, the closer should the behavior of the system approach plug flow. This will be shown to be so.

Let us now quantitatively evaluate the behavior of a series of N equal-size mixed flow reactors. Density changes will be assumed to be negligible; hence $\varepsilon = 0$ and $t = \tau$. As a rule, with mixed flow reactors it is more convenient to develop the necessary equations in terms of concentrations rather than fractional conversions; therefore, we use this approach. The nomenclature used is shown in Fig. 6.4 with subscript i referring to the i th vessel.

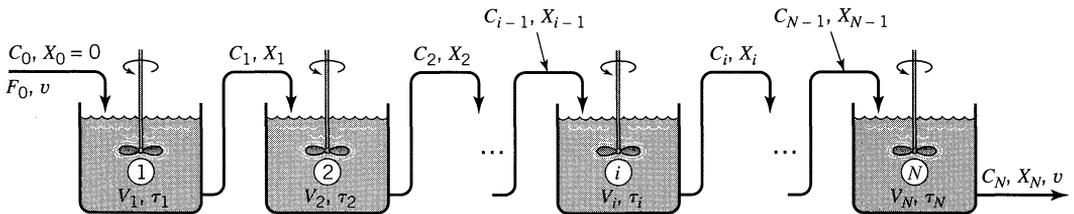


Figure 6.4 Notation for a system of N equal-size mixed reactors in series.

First-Order Reactions. From Eq. 5.12 a material balance for component A about vessel i gives

$$\tau_i = \frac{C_0 V_i}{F_0} = \frac{V_i}{v} = \frac{C_0(X_i - X_{i-1})}{-r_{Ai}}$$

Because $\varepsilon = 0$ this may be written in terms of concentrations. Hence

$$\tau_i = \frac{C_0[(1 - C_i/C_0) - (1 - C_{i-1}/C_0)]}{kC_i} = \frac{C_{i-1} - C_i}{kC_i}$$

or

$$\frac{C_{i-1}}{C_i} = 1 + k\tau_i \quad (5)$$

Now the space-time τ (or mean residence time t) is the same in all the equal-size reactors of volume V_i . Therefore,

$$\frac{C_0}{C_N} = \frac{1}{1 - X_N} = \frac{C_0 C_1}{C_1 C_2} \cdots \frac{C_{N-1}}{C_N} = (1 + k\tau_i)^N \quad (6a)$$

Rearranging, we find for the system as a whole

$$\tau_{N \text{ reactors}} = N\tau_i = \frac{N}{k} \left[\left(\frac{C_0}{C_N} \right)^{1/N} - 1 \right] \quad (6b)$$

In the limit, for $N \rightarrow \infty$, this equation reduces to the plug flow equation

$$\tau_p = \frac{1}{k} \ln \frac{C_0}{C} \quad (7)$$

With Eqs. 6b and 7 we can compare performance of N reactors in series with a plug flow reactor or with a single mixed flow reactor. This comparison is shown in Fig. 6.5 for first-order reactions in which density variations are negligible.

Second-Order Reactions. We may evaluate the performance of a series of mixed flow reactors for a second-order, bimolecular-type reaction, no excess of either reactant, by a procedure similar to that of a first-order reaction. Thus, for

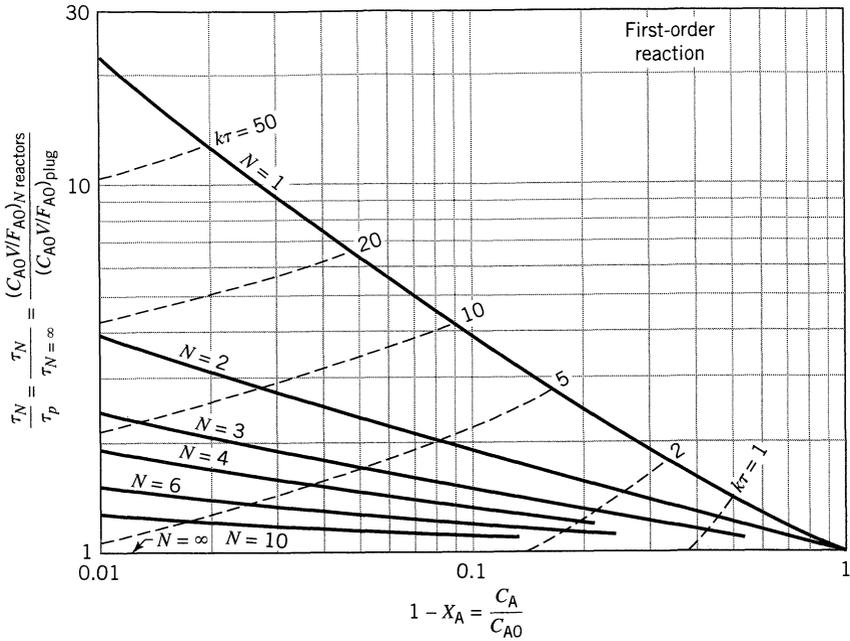
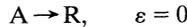


Figure 6.5 Comparison of performance of a series of N equal-size mixed flow reactors with a plug flow reactor for the first-order reaction



For the same processing rate of identical feed the ordinate measures the volume ratio V_N/V_p directly.

N reactors in series we find

$$C_N = \frac{1}{4k\tau_i} \left(-2 + 2 \sqrt{-1 \dots + 2 \sqrt{-1 + 2 \sqrt{1 + 4C_0k\tau_i}}} \right) \quad (8a)$$

whereas for plug flow

$$\frac{C_0}{C} = 1 + C_0k\tau_p \quad (8b)$$

A comparison of the performance of these reactors is shown in Fig. 6.6.

Figures 6.5 and 6.6 support our intuition by showing that the volume of system required for a given conversion decreases to plug flow volume as the number of reactors in series is increased, the greatest change taking place with the addition of a second vessel to a one-vessel system.

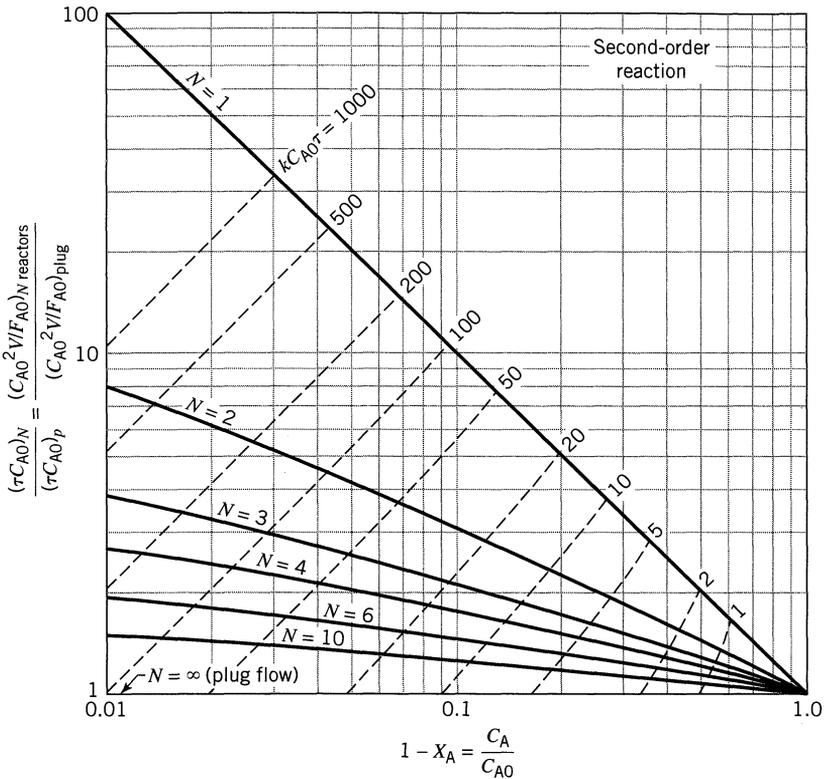
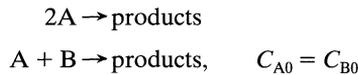


Figure 6.6 Comparison of performance of a series of N equal-size mixed flow reactors with a plug flow reactor for elementary second-order reactions



with negligible expansion. For the same processing rate of identical feed the ordinate measures the volume ratio V_N/V_p or space-time ratio τ_N/τ_p directly.

EXAMPLE 6.2 MIXED FLOW REACTORS IN SERIES

At present 90% of reactant A is converted into product by a second-order reaction in a single mixed flow reactor. We plan to place a second reactor similar to the one being used in series with it.

- For the same treatment rate as that used at present, how will this addition affect the conversion of reactant?
- For the same 90% conversion, by how much can the treatment rate be increased?

SOLUTION

The sketch of Fig. E6.2 shows how the performance chart of Fig. 6.6 can be used to help solve this problem.

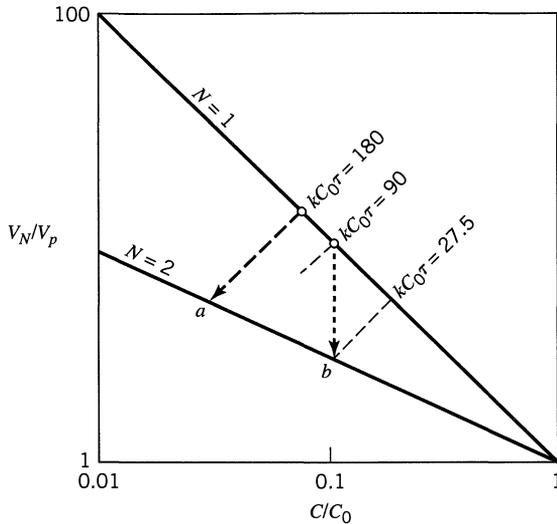


Figure E6.2

(a) Find the conversion for the same treatment rate. For the single reactor at 90% conversion we have from Fig. 6.6

$$kC_0\tau = 90$$

For the two reactors the space-time or holding time is doubled; hence, the operation will be represented by the dashed line of Fig. 6.6 where

$$kC_0\tau = 180$$

This line cuts the $N = 2$ line at a conversion $X = 97.4\%$, point *a*.

(b) Find the treatment rate for the same conversion. Staying on the 90% conversion line, we find for $N = 2$ that

$$kC_0\tau = 27.5, \quad \text{point } b$$

Comparing the value of the reaction rate group for $N = 1$ and $N = 2$, we find

$$\frac{(kC_0\tau)_{N=2}}{(kC_0\tau)_{N=1}} = \frac{\tau_{N=2}}{\tau_{N=1}} = \frac{(V/v)_{N=2}}{(V/v)_{N=1}} = \frac{27.5}{90}$$

Since $V_{N=2} = 2V_{N=1}$ the ratio of flow rates becomes

$$\frac{v_{N=1}}{v_{N=1}} = \frac{90}{27.5} (2) = 6.6$$

Thus, the treatment rate can be raised to 6.6 times the original.

Note. If the second reactor had been operated in parallel with the original unit then the treatment rate could only be doubled. Thus, there is a definite advantage in operating these two units in series. This advantage becomes more pronounced at higher conversions.

Mixed Flow Reactors of Different Sizes in Series

For arbitrary kinetics in mixed flow reactors of different size, two types of questions may be asked: how to find the outlet conversion from a given reactor system, and the inverse question, how to find the best setup to achieve a given conversion. Different procedures are used for these two problems. We treat them in turn.

Finding the Conversion in a Given System A graphical procedure for finding the outlet composition from a series of mixed flow reactors of various sizes for reactions with negligible density change has been presented by Jones (1951). All that is needed is an r versus C curve for component A to represent the reaction rate at various concentrations.

Let us illustrate the use of this method by considering three mixed flow reactors in series with volumes, feed rates, concentrations, space-times (equal to residence times because $\varepsilon = 0$), and volumetric flow rates as shown in Fig. 6.7. Now from Eq. 5.11, noting that $\varepsilon = 0$, we may write for component A in the first reactor

$$\tau_1 = \bar{t}_1 = \frac{V_1}{v} = \frac{C_0 - C_1}{(-r)_1}$$

or

$$-\frac{1}{\tau_1} = \frac{(-r)_1}{C_1 - C_0} \quad (9)$$

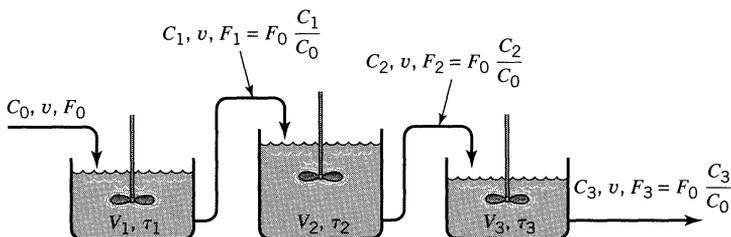


Figure 6.7 Notation for a series of unequal-size mixed flow reactors.

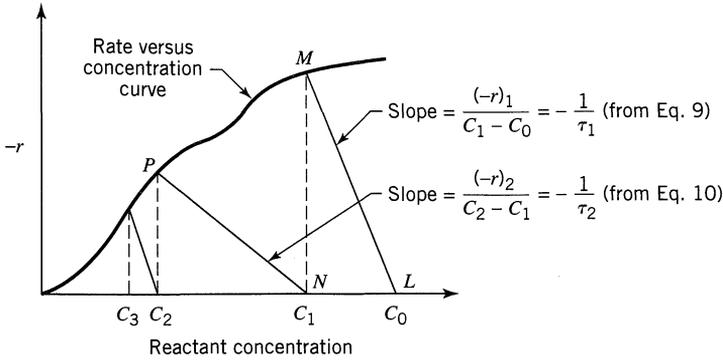


Figure 6.8 Graphical procedure for finding compositions in a series of mixed flow reactors.

Similarly, from Eq. 5.12 for the i th reactor we may write

$$-\frac{1}{\tau_i} = \frac{(-r)_i}{C_i - C_{i-1}} \quad (10)$$

Plot the C versus r curve for component A and suppose that it is as shown in Fig. 6.8. To find the conditions in the first reactor note that the inlet concentration C_0 is known (point L), that C_1 and $(-r)_1$ correspond to a point on the curve to be found (point M), and that the slope of the line $LM = MN/NL = (-r)_1 / (C_1 - C_0) = -(1/\tau_1)$ from Eq. 6.9. Hence, from C_0 draw a line of slope $-(1/\tau_1)$ until it cuts the rate curve; this gives C_1 . Similarly, we find from Eq. 6.10 that a line of slope $-(1/\tau_2)$ from point N cuts the curve at P , giving the concentration C_2 of material leaving the second reactor. This procedure is then repeated as many times as needed.

With slight modification this graphical method can be extended to reactions in which density changes are appreciable.

Determining the Best System for a Given Conversion. Suppose we want to find the minimum size of two mixed flow reactors in series to achieve a specified conversion of feed which reacts with arbitrary but known kinetics. The basic performance expressions, Eqs. 5.11 and 5.12, then give, in turn, for the first reactor

$$\tau_1 = \frac{X_1}{(-r)_1} \quad (11)$$

and for the second reactor

$$\tau_2 = \frac{X_2 - X_1}{(-r)_2} \quad (12)$$

These relationships are displayed in Fig. 6.9 for two alternative reactor arrangements, both giving the same final conversion X_2 . Note, as the intermediate

This area is maximized when

$$dA = 0 = y dx + x dy$$

or when

$$-\frac{dy}{dx} = \frac{y}{x} \quad (14)$$

In words, this condition means that the area is maximized when M is at that point where the slope of the curve equals the slope of the diagonal NL of the rectangle. Depending on the shape of the curve, there may be more than one or there may be no “best” point. However, for n th-order kinetics, $n > 0$, there always is just one “best” point.

We will use this method of maximizing a rectangle in later chapters. But let us return to our problem.

The optimum size ratio of the two reactors is achieved where the slope of the rate curve at M equals the diagonal NL . The best value of M is shown in Fig. 6.11, and this determines the intermediate conversion X_1 as well as the size of units needed.

The optimum size ratio for two mixed flow reactors in series is found in general to be dependent on the kinetics of the reaction and on the conversion level. For the special case of first-order reactions equal-size reactors are best; for reaction orders $n > 1$ the smaller reactor should come first; for $n < 1$ the larger should come first (see Problem 6.3). However, Szepe and Levenspiel (1964) show that the advantage of the minimum size system over the equal-size system is quite small, only a few percent at most. Hence, overall economic consideration would nearly always recommend using equal-size units.

The above procedure can be extended directly to multistage operations; however, here the argument for equal-size units is stronger still than for the two-stage system.

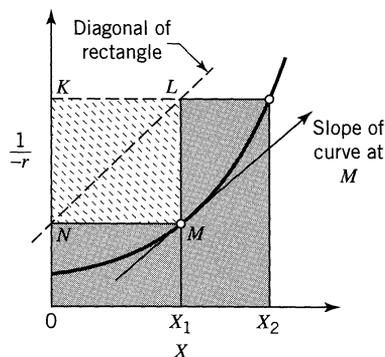


Figure 6.11 Maximization of rectangles applied to find the optimum intermediate conversion and optimum sizes of two mixed flow reactors in series.

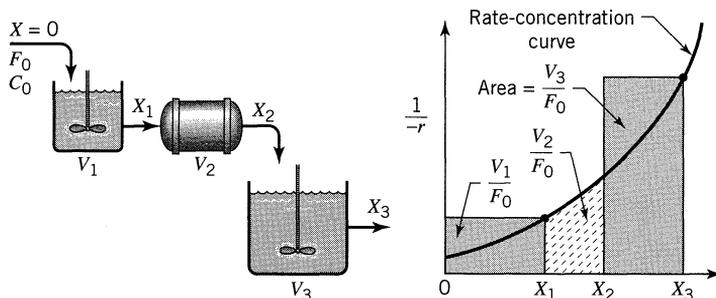


Figure 6.12 Graphical design procedure for reactors in series.

Reactors of Different Types in Series

If reactors of different types are put in series, such as a mixed flow reactor followed by a plug flow reactor which in turn is followed by another mixed flow reactor, we may write for the three reactors

$$\frac{V_1}{F_0} = \frac{X_1 - X_0}{(-r)_1}, \quad \frac{V_2}{F_0} = \int_{x_1}^{x_2} \frac{dX}{-r}, \quad \frac{V_3}{F_0} = \frac{X_3 - X_2}{(-r)_3}$$

These relationships are represented in graphical form in Fig. 6.12. This allows us to predict the overall conversions for such systems, or conversions at intermediate points between the individual reactors. These intermediate conversions may be needed to determine the duty of interstage heat exchangers.

Best Arrangement of a Set of Ideal Reactors. For the most effective use of a given set of ideal reactors we have the following general rules:

1. For a reaction whose rate-concentration curve rises monotonically (any n th-order reaction, $n > 0$) the reactors should be connected in series. They should be ordered so as to keep the concentration of reactant as high as possible if the rate-concentration curve is concave ($n > 1$), and as low as possible if the curve is convex ($n < 1$). As an example, for the case of Fig. 6.12 the ordering of units should be plug, small mixed, large mixed, for $n > 1$; the reverse order should be used when $n < 1$.
2. For reactions where the rate-concentration curve passes through a maximum or minimum the arrangement of units depends on the actual shape of curve, the conversion level desired, and the units available. No simple rules can be suggested.
3. Whatever may be the kinetics and the reactor system, an examination of the $1/(-r_A)$ vs. C_A curve is a good way to find the best arrangement of units.

The problems at the end of this chapter illustrate these findings.

6.3 RECYCLE REACTOR

In certain situations it is found to be advantageous to divide the product stream from a plug flow reactor and return a portion of it to the entrance of the reactor. Let the *recycle ratio* R be defined as

$$R = \frac{\text{volume of fluid returned to the reactor entrance}}{\text{volume leaving the system}} \quad (15)$$

This recycle ratio can be made to vary from zero to infinity. Reflection suggests that as the recycle ratio is raised the behavior shifts from plug flow ($R = 0$) to mixed flow ($R = \infty$). Thus, recycling provides a means for obtaining various degrees of backmixing with a plug flow reactor. Let us develop the performance equation for the recycle reactor.

Consider a recycle reactor with nomenclature as shown in Fig. 6.13. Across the reactor itself Eq. 5.18 for plug flow gives

$$\frac{V}{F'_{A0}} = \int_{X_{A1}}^{X_{A2}=X_{Af}} \frac{dX_A}{-r_A} \quad (16)$$

where F'_{A0} would be the feed rate of A if the stream entering the reactor (fresh feed plus recycle) were unconverted. Since F'_{A0} and X_{A1} are not known directly, they must be written in terms of known quantities before Eq. 16 can be used. Let us now do this.

The flow entering the reactor includes both fresh feed and the recycle stream. Measuring the flow split at point L (point K will not do if $\varepsilon \neq 0$) we then have

$$\begin{aligned} F'_{A0} &= \left(\begin{array}{l} \text{A which would enter in an} \\ \text{unconverted recycle stream} \end{array} \right) + \left(\begin{array}{l} \text{A entering in} \\ \text{fresh feed} \end{array} \right) \\ &= RF_{A0} + F_{A0} = (R + 1)F_{A0} \end{aligned} \quad (17)$$

Now to the evaluation of X_{A1} : from Eq. 4.5 we may write

$$X_{A1} = \frac{1 - C_{A1}/C_{A0}}{1 + \varepsilon_A C_{A1}/C_{A0}} \quad (18)$$

Because the pressure is taken to be constant, the streams meeting at point K may be added directly. This gives

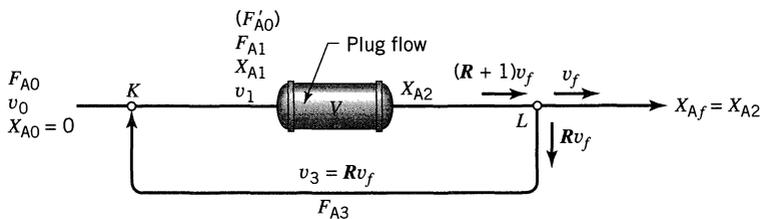


Figure 6.13 Nomenclature for the recycle reactor.

$$C_{A1} = \frac{F_{A1}}{v_1} = \frac{F_{A0} + F_{A3}}{v_0 + Rv_f} = \frac{F_{A0} + RF_{A0}(1 - X_{Af})}{v_0 + Rv_0(1 + \varepsilon_A X_{Af})} = C_{A0} \left(\frac{1 + R - RX_{Af}}{1 + R + R\varepsilon_A X_{Af}} \right) \quad (19)$$

Combining Eqs. 18 and 19 gives X_{A1} in terms of measured quantities, or

$$X_{A1} = \left(\frac{R}{R+1} \right) X_{Af} \quad (20)$$

Finally, on replacing Eqs. 17 and 20 in Eq. 16 we obtain the useful form for the performance equation for recycle reactors, good for any kinetics, any ε value and for $X_{A0} = 0$.

$$\frac{V}{F_{A0}} = (R+1) \int_{\left(\frac{R}{R+1}\right) X_{Af}}^{X_{Af}} \frac{dX_A}{-r_A} \quad \dots \text{any } \varepsilon_A \quad (21)$$

For the special case where density changes are negligible we may write this equation in terms of concentrations, or

$$\tau = \frac{C_{A0}V}{F_{A0}} = -(R+1) \int_{\frac{C_{A0} + RC_{Af}}{R+1}}^{C_{Af}} \frac{dC_A}{-r_A} \quad \dots \varepsilon_A = 0 \quad (22)$$

These expressions are represented graphically in Fig. 6.14.

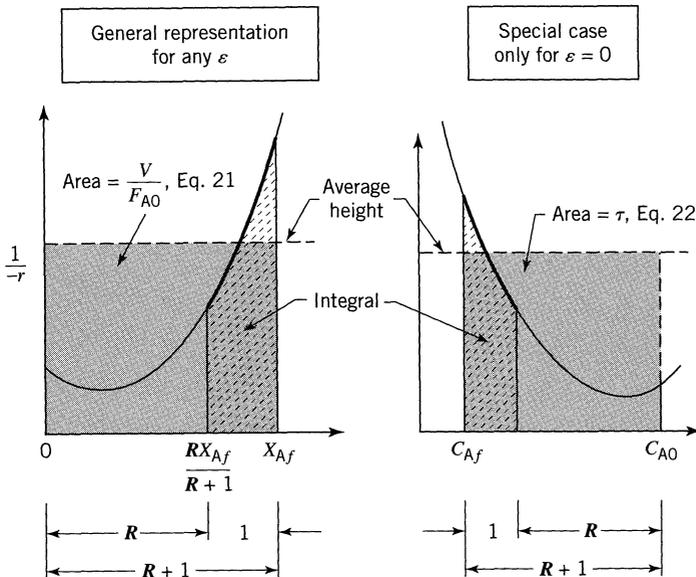


Figure 6.14 Representation of the performance equation for recycle reactors.

For the extremes of negligible and infinite recycle the system approaches plug flow and mixed flow, or

$$\frac{V}{F_{A0}} = (R + 1) \int_{\frac{R}{R+1} X_{Af}}^{X_{Af}} \frac{dX_A}{-r_A}$$

$R = 0$
 \downarrow
 $\frac{V}{F_{A0}} = \int_A^{X_{Af}} \frac{dX_A}{-r_A}$

 plug flow

$R = \infty$
 \downarrow
 $\frac{V}{F_{A0}} = \frac{X_{Af}}{-r_{Af}}$

 mixed flow

The approach to these extremes is shown in Fig. 6.15.

Integration of the recycle equation gives, for *first-order reaction*, $\varepsilon_A = 0$,

$$\frac{k\tau}{R + 1} = \ln \left[\frac{C_{A0} + RC_{Af}}{(R + 1)C_{Af}} \right] \quad (23)$$

and for *second-order reaction*, $2A \rightarrow$ products, $-r_A = kC_A^2$, $\varepsilon_A = 0$,

$$\frac{kC_{A0}\tau}{R + 1} = \frac{C_{A0}(C_{A0} - C_{Af})}{C_{Af}(C_{A0} + RC_{Af})} \quad (24)$$

The expressions for $\varepsilon_A \neq 0$ and for other reaction orders can be evaluated, but are more cumbersome.

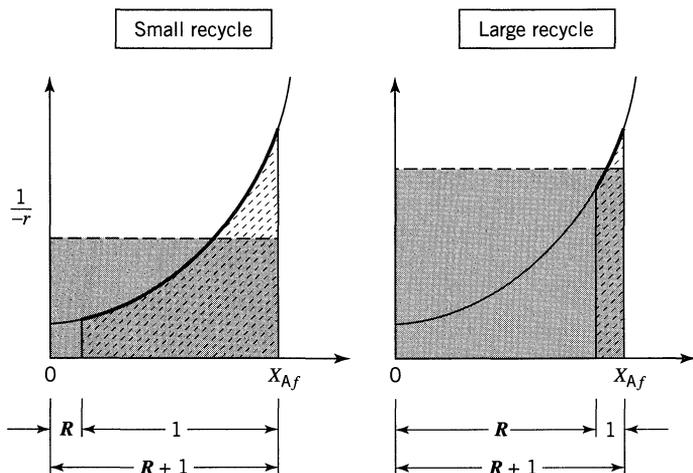


Figure 6.15 The recycle extremes approach plug flow ($R \rightarrow 0$) and mixed flow ($R \rightarrow \infty$).

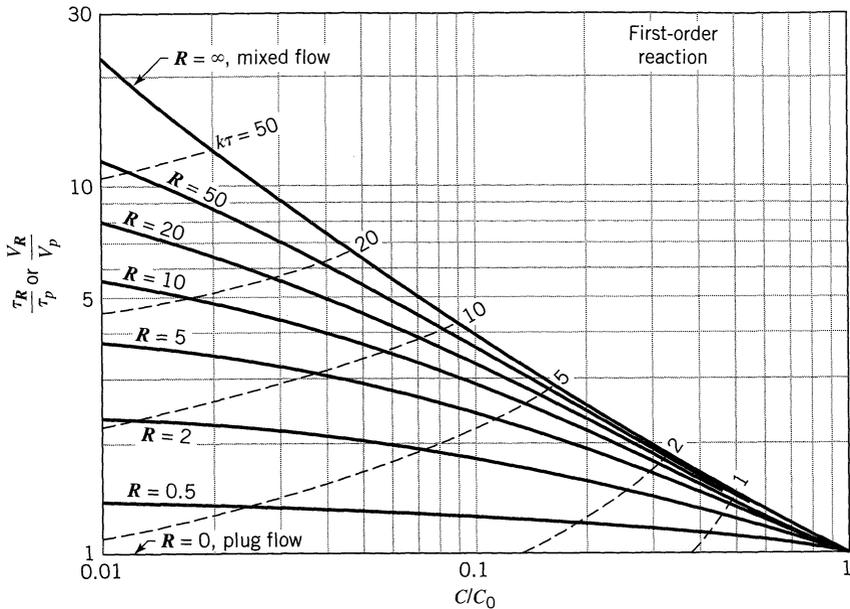


Figure 6.16 Comparison of performance of recycle and plug flow for first-order reactions



Figures 6.16 and 6.17 show the transition from plug to mixed flow as R increases, and a match of these curves with those for N tanks in series (Figs. 6.5 and 6.6) gives the following rough comparison for equal performance:

No. of tanks	R for first-order reaction			R for second-order reaction		
	at $X_A = 0.5$	0.90	0.99	at $X_A = 0.5$	0.90	0.99
1	∞	∞	∞	∞	∞	∞
2	1.0	2.2	5.4	1.0	2.8	7.5
3	0.5	1.1	2.1	0.5	1.4	2.9
4	0.33	0.68	1.3	0.33	0.90	1.7
10	0.11	0.22	0.36	0.11	0.29	0.5
∞	0	0	0	0	0	0

The recycle reactor is a convenient way for approaching mixed flow with what is essentially a plug flow device. Its particular usefulness is with solid catalyzed reactions with their fixed bed contactors. We meet this and other applications of recycle reactors in later chapters.

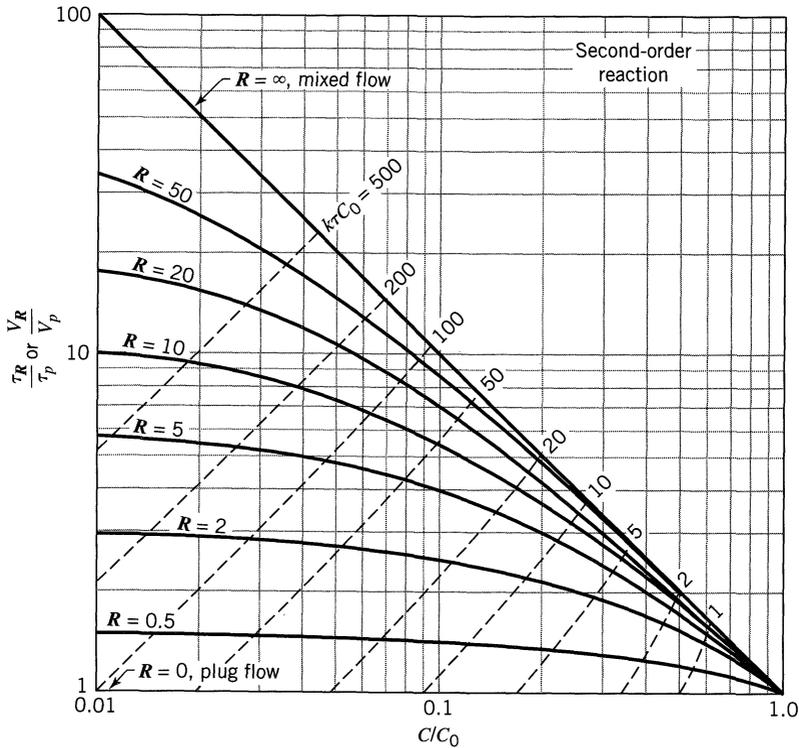
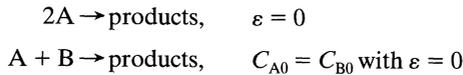


Figure 6.17 Comparison of performance of recycle reactors with plug flow reactors for elementary second-order reactions (Personal communication, from T. J. Fitzgerald and P. Filleli):



6.4 AUTOCATALYTIC REACTIONS

When a material reacts away by any n th order rate ($n > 0$) in a batch reactor, its rate of disappearance is rapid at the start when the concentration of reactant is high. This rate then slows progressively as reactant is consumed. In an autocatalytic reaction, however, the rate at the start is low because little product is present; it increases to a maximum as product is formed and then drops again to a low value as reactant is consumed. Figure 6.18 shows a typical situation.

Reactions with such rate-concentration curves lead to interesting optimization problems. In addition, they provide a good illustration of the general design method presented in this chapter. For these reasons let us examine these reactions in some detail. In our approach we deal exclusively with their $1/(-r_A)$ versus X_A curves with their characteristic minima, as shown in Fig. 6.18.

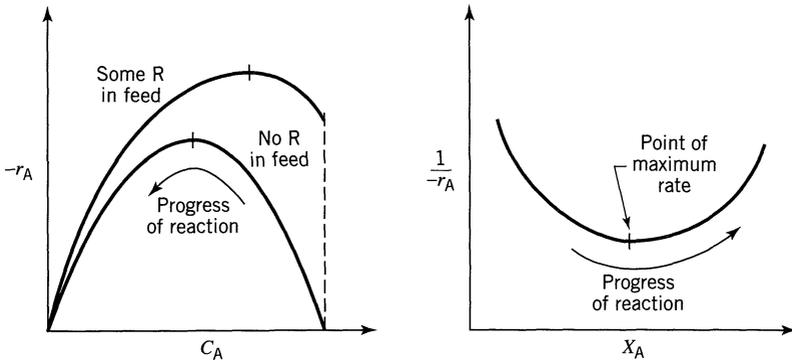
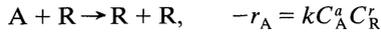


Figure 6.18 Typical rate-concentration curve for autocatalytic reactions, for example:



Plug Flow Versus Mixed Flow Reactor, No Recycle. For any particular rate-concentration curve a comparison of areas in Fig. 6.19 will show which reactor is superior (which requires a smaller volume) for a given job. We thus find

1. At low conversion the mixed reactor is superior to the plug flow reactor.
2. At high enough conversions the plug flow reactor is superior.

These findings differ from ordinary n th-order reactions ($n > 0$) where the plug flow reactor is always more efficient than the mixed flow reactor. In addition, we should note that a plug flow reactor will not operate at all with a feed of pure reactant. In such a situation the feed must be continually primed with product, an ideal opportunity for using a recycle reactor.

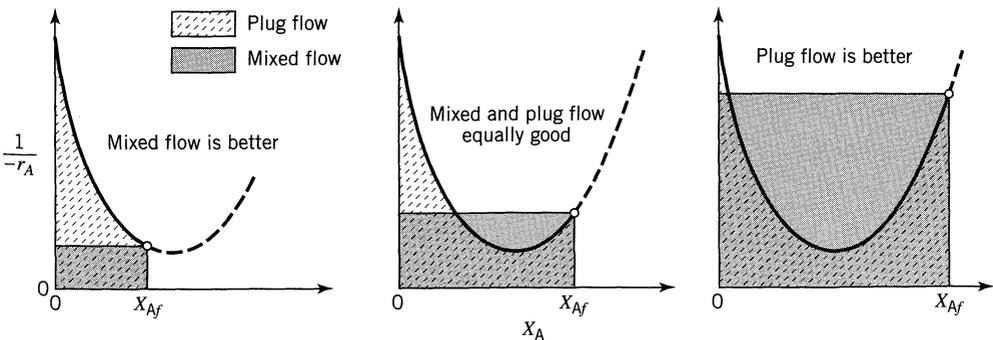


Figure 6.19 For autocatalytic reactions mixed flow is more efficient at low conversions, plug flow is more efficient at high conversions.

Optimum Recycle Operations. When material is to be processed to some fixed final conversion X_{Af} in a recycle reactor, reflection suggests that there must be a particular recycle ratio which is optimum in that it minimizes the reactor volume or space-time. Let us determine this value of R .

The *optimum recycle ratio* is found by differentiating Eq. 21 with respect to R and setting to zero, thus

$$\text{take } \frac{d(\tau/C_{A0})}{dR} = 0 \quad \text{for} \quad \frac{\tau}{C_{A0}} = \int_{X_{Ai} = \frac{RX_{Af}}{R+1}}^{X_{Af}} \frac{R+1}{(-r_A)} dX_A \quad (25)$$

This operation requires differentiating under an integral sign. From the theorems of calculus, if

$$F(R) = \int_{a(R)}^{b(R)} f(x, R) dx \quad (26)$$

then

$$\frac{dF}{dR} = \int_{a(R)}^{b(R)} \frac{\partial f(x, R)}{\partial R} dx + f(b, R) \frac{db}{dR} - f(a, R) \frac{da}{dR} \quad (27)$$

For our case, Eq. 25, we then find

$$\frac{d(\tau/C_{A0})}{dR} = 0 = \int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{(-r_A)} + 0 - \frac{R+1}{(-r_A)} \Big|_{X_{Ai}} \frac{dX_{Ai}}{dR}$$

where

$$\frac{dX_{Ai}}{dR} = \frac{X_{Af}}{(R+1)^2}$$

Combining and rearranging then gives for the optimum

$$\boxed{\frac{1}{-r_A} \Big|_{X_{Ai}} = \frac{\int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{-r_A}}{(X_{Af} - X_{Ai})}} \quad (28)$$

In words, the optimum recycle ratio introduces to the reactor a feed whose $1/(-r_A)$ value (KL in Fig. 6.20) equals the average $1/(-r_A)$ value in the reactor as a whole (PQ in Fig. 6.20). Figure 6.20 compares this optimum with conditions where the recycle is either too high or too low.

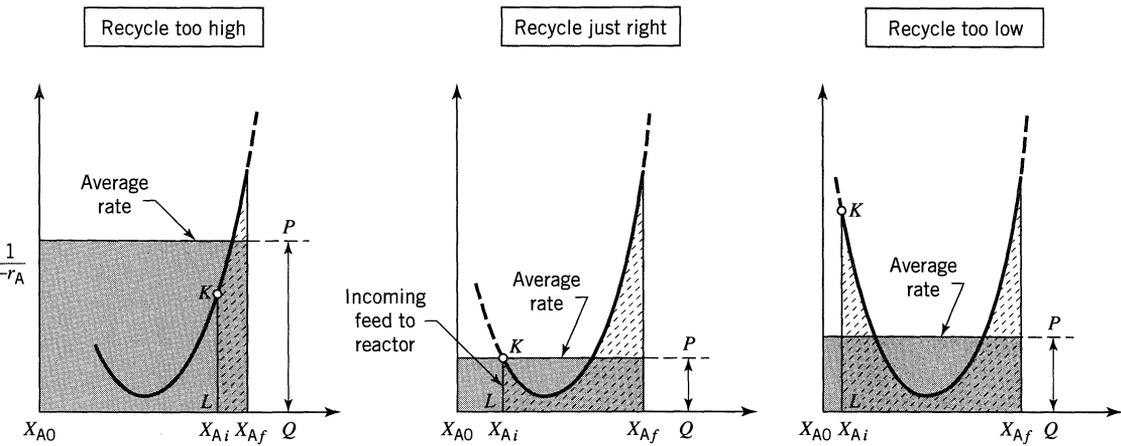


Figure 6.20 Correct recycle ratio for an autocatalytic reaction compared with recycle ratios which are too high and too low.

Occurrence of Autocatalytic Reactions. The most important examples of autocatalytic reactions are the broad class of fermentation reactions which result from the reaction of microorganism on an organic feed. When they can be treated as single reactions, the methods of this chapter can be applied directly. Another type of reaction which has autocatalytic behavior is the exothermic reaction (say, the combustion of fuel gas) proceeding in an adiabatic manner with cool reactants entering the system. In such a reaction, called *autothermal*, heat may be considered to be the product which sustains the reaction. Thus, with plug flow the reaction will die. With backmixing the reaction will be self-sustaining because the heat generated by the reaction can raise fresh reactants to a temperature at which they will react. Autothermal reactions are of great importance in solid catalyzed gas-phase systems and are treated later in the book.

Reactor Combinations

For autocatalytic reactions all sorts of reactor arrangements are to be considered if product recycle or product separation with recycle is allowable. In general, for a rate-concentration curve as shown in Fig. 6.21 one should always try to reach point *M* in one step (using mixed flow in a single reactor), then follow with plug flow or as close to plug flow as possible. This procedure is shown as the shaded area in Fig. 6.21a.

When separation and reuse of unconverted reactant is possible, operate at point *M* (see Fig. 6.21b).

The volume required is now the very minimum, less than any of the previous ways of operating. However, the overall economics, including the cost of separation and of recycle, will determine which scheme is the optimum overall.

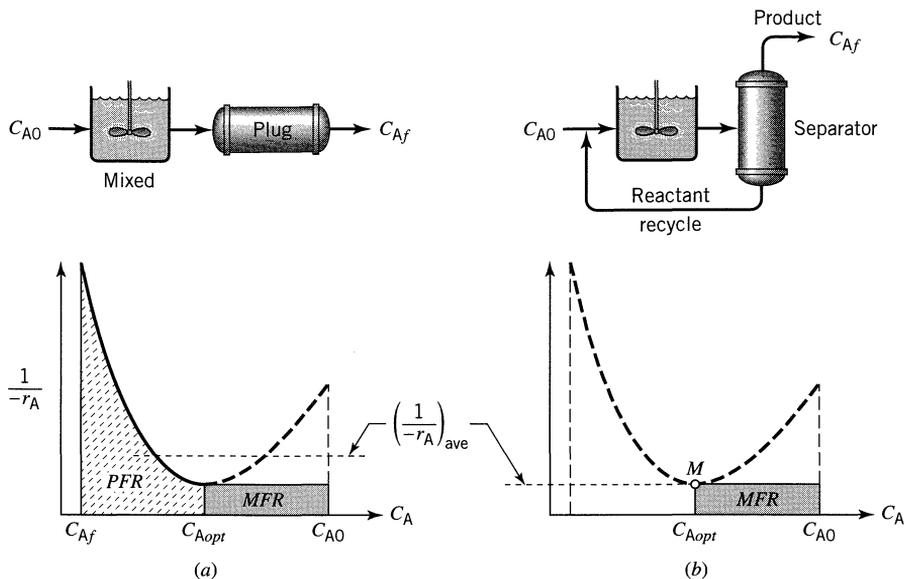


Figure 6.21 (a) The best multiple reactor scheme. (b) The best scheme when unconverted reactant can be separated and recycled.

EXAMPLE 6.3 FINDING THE BEST REACTOR SETUP

In the presence of a specific enzyme E, which acts as a homogeneous catalyst, a harmful organic A present in industrial waste water degrades into harmless chemicals. At a given enzyme concentration C_E tests in a laboratory mixed flow reactor give the following results:

C_{A0} , mmol/m ³	2	5	6	6	11	14	16	24
C_A , mmol/m ³	0.5	3	1	2	6	10	8	4
τ , min	30	1	50	8	4	20	20	4

We wish to treat 0.1 m³/min of this waste water having $C_{A0} = 10$ mmol/m³ to 90% conversion with this enzyme at concentration C_E .

- One possibility is to use a long tubular reactor (assume plug flow) with possible recycle of exit fluid. What design do you recommend? Give the size of the reactor, tell if it should be used with recycle, and if so determine the recycle flow rate in cubic meters per minute (m³/min). Sketch your recommended design.
- Another possibility is to use one or two stirred tanks (assume ideal). What two-tank design do you recommend, and how much better is it than the one-tank arrangement?
- What arrangement of plug flow and mixed flow reactors would you use to minimize the total volume of reactors needed? Sketch your recommended design and show the size of units selected. We should mention that separation and recycle of part of the product stream is not allowed.

SOLUTION

First calculate and tabulate $1/-r_A$ at the measured C_A . This is shown as the last line of Table E6.3. Next, draw the $1/-r_A$ vs. C_A curve. This is seen to be U-shaped (see Figs. E6.3a, b, c) so we must prepare to deal with an autocatalytic type reacting system.

Table E6.3

$C_{A0}, \text{mmol/m}^3$	2	5	6	6	11	14	16	24
$C_A, \text{mmol/m}^3$	0.5	3	1	2	6	10	8	4
τ, min	30	1	50	8	4	20	20	4
$\frac{1}{-r_A} = \frac{\tau}{C_{A0} - C_A}, \frac{\text{m}^3 \cdot \text{min}}{\text{mmol}}$	20	0.5	10	2	0.8	5	2.5	0.2

Part (a) Solution. From the $-1/r_A$ vs. C_A curve we see that we should use plug flow with recycle. From Fig. E6.3a we find

$$C_{Ain} = 6.6 \text{ mmol/m}^3$$

$$R = \frac{10 - 6.6}{6.6 - 1} = 0.607$$

$$V = \tau v_0 = \text{area}(v_0) = [(10 - 1)(1.2)](0.1) = \underline{\underline{1.08 \text{ m}^3}}$$

$$v_R = v_0 R = 0.1(0.607) = \underline{\underline{0.0607 \text{ m}^3/\text{min}}}$$

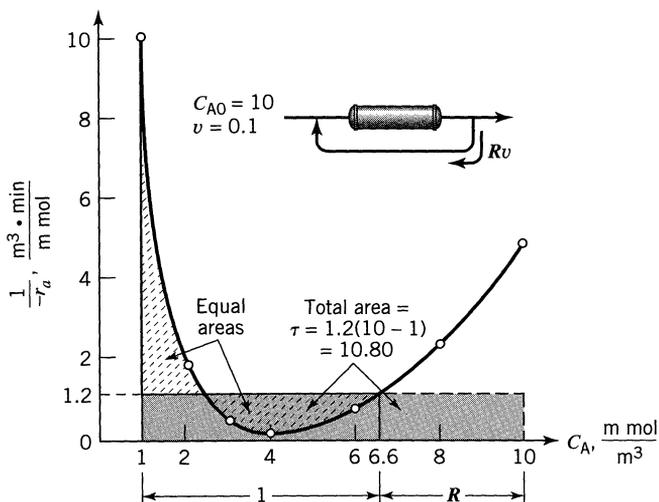


Figure E6.3a Plug flow with recycle.

Part (b) Solution. Drawing slopes and diagonals according to the method of maximization of rectangles we end up with Fig. E6.3b.

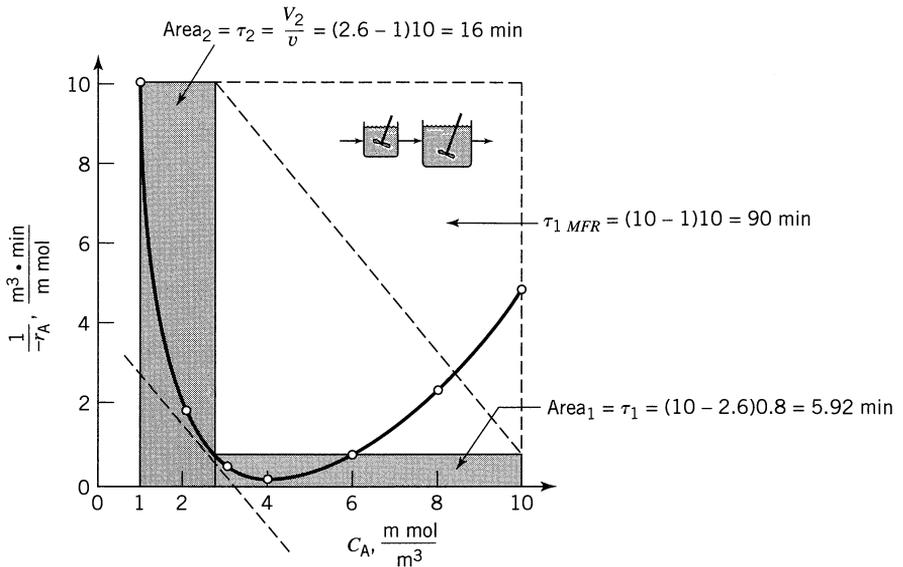


Figure E6.3b One and two mixed flow reactors in series.

For 1 tank $V = \tau v = 90(0.1) = \underline{\underline{9.0 \text{ m}^3}}$

For 2 tanks $\left. \begin{aligned} V_1 &= \tau_1 v = 5.92(0.1) = 0.59 \\ V_2 &= \tau_2 v = 16(0.1) = 1.6 \text{ m}^3 \end{aligned} \right\} V_{\text{total}} = \underline{\underline{2.19 \text{ m}^3}}$

Part (c) Solution. Following the reasoning in this chapter we should use a mixed flow reactor followed by a plug flow reactor. So with Fig. E6.3c we find

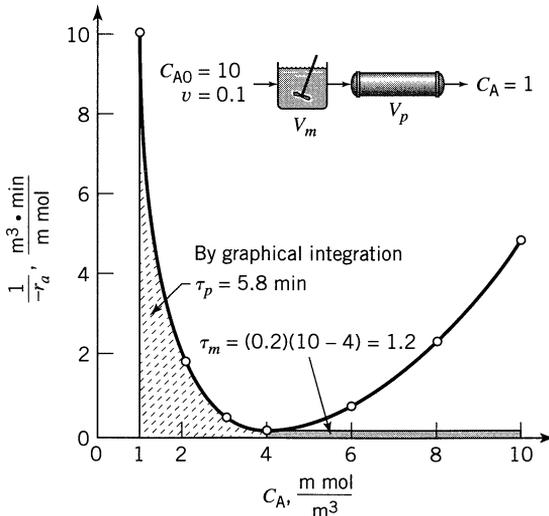


Figure E6.3c Arrangement with smallest volume.

$$\left. \begin{array}{l} \text{For the MFR } V_m = v\tau_m = 0.1(1.2) = 0.12 \text{ m}^3 \\ \text{For the PFR } V_p = v\tau_p = 0.1(5.8) = 0.58 \text{ m}^3 \end{array} \right\} V_{\text{total}} = \underline{\underline{0.7 \text{ m}^3}}$$

Note which scheme (a) or (b) or (c) gives the smallest size of reactors.

REFERENCES

- Jones, R. W., *Chem. Eng. Progr.*, **47**, 46 (1951).
 Szepe, S., and O. Levenspiel, *Ind. Eng. Chem. Process Design Develop.*, **3**, 214 (1964).

PROBLEMS

- 6.1.** A liquid reactant stream (1 mol/liter) passes through two mixed flow reactors in a series. The concentration of A in the exit of the first reactor is 0.5 mol/liter. Find the concentration in the exit stream of the second reactor. The reaction is second-order with respect to A and $V_2/V_1 = 2$.
- 6.2.** Water containing a short-lived radioactive species flows continuously through a well-mixed holdup tank. This gives time for the radioactive material to decay into harmless waste. As it now operates, the activity of the exit stream is 1/7 of the feed stream. This is not bad, but we'd like to lower it still more.
 One of our office secretaries suggests that we insert a baffle down the middle of the tank so that the holdup tank acts as two well-mixed tanks in series. Do you think this would help? If not, tell why; if so, calculate the expected activity of the exit stream compared to the entering stream.
- 6.3.** An aqueous reactant stream (4 mol A/liter) passes through a mixed flow reactor followed by a plug flow reactor. Find the concentration at the exit of the plug flow reactor if in the mixed flow reactor $C_A = 1$ mol/liter. The reaction is second-order with respect to A, and the volume of the plug flow unit is three times that of the mixed flow unit.
- 6.4.** Reactant A ($A \rightarrow R$, $C_{A0} = 26$ mol/m³) passes in steady flow through four equal-size mixed flow reactors in series ($\tau_{\text{total}} = 2$ min). When steady state is achieved the concentration of A is found to be 11, 5, 2, 1 mol/m³ in the four units. For this reaction, what must be τ_{plug} so as to reduce C_A from $C_{A0} = 26$ to $C_{Af} = 1$ mol/m³?
- 6.5.** Originally we had planned to lower the activity of a gas stream containing radioactive Xe-138 (half-life = 14 min) by having it pass through two holdup tanks in series, both well mixed and of such size that the mean residence time of gas is 2 weeks in each tank. It has been suggested that we replace the two tanks with a long tube (assume plug flow). What must be the size of this tube compared to the two original stirred tanks, and

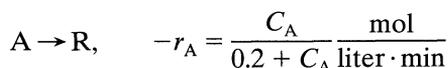
what should be the mean residence time of gas in this tube for the same extent of radioactive decay?

- 6.6. At 100°C pure gaseous A reacts away with stoichiometry $2A \rightarrow R + S$ in a constant volume batch reactor as follows:

t, sec	0	20	40	60	80	100	120	140	160
p_A, atm	1.00	0.96	0.80	0.56	0.32	0.18	0.08	0.04	0.02

What size of plug flow reactor operating at 100°C and 1 atm can treat 100 moles A/hr in a feed consisting of 20% inerts to obtain 95% conversion of A?

- 6.7. We wish to treat 10 liters/min of liquid feed containing 1 mol A/liter to 99% conversion. The stoichiometry and kinetics of the reaction are given by



Suggest a good arrangement for doing this using two mixed flow reactors, and find the size of the two units needed. Sketch the final design chosen.

- 6.8. From steady-state kinetics runs in a mixed flow reactor, we obtain the following data on the reaction $A \rightarrow R$.

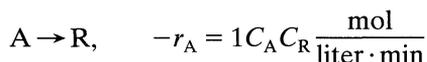
τ, sec	$C_{A0}, \text{mmol/liter}$	$C_A, \text{mmol/liter}$
60	50	20
35	100	40
11	100	60
20	200	80
11	200	100

Find the space time needed to treat a feed of $C_{A0} = 100$ mmol/liter to 80% conversion

- (a) in a plug flow reactor.
(b) in a mixed flow reactor.

- 6.9. At present we have 90% conversion of a liquid feed ($n = 1$, $C_{A0} = 10$ mol/liter) to our plug flow reactor with recycle of product ($R = 2$). If we shut off the recycle stream, by how much will this lower the processing rate of our feed to the same 90% conversion?

- 6.10. Aqueous feed containing reactant A ($C_{A0} = 2$ mol/liter) enters a plug flow reactor (10 liter) which has a provision for recycling a portion of the flowing stream. The reaction kinetics and stoichiometry are

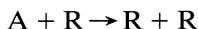


and we wish to get 96% conversion. Should we use the recycle stream? If so, at what value should we set the recycle flow rate so as to obtain the highest production rate, and what volumetric feed rate can we process to this conversion in the reactor?

- 6.11.** Consider the autocatalytic reaction $A \rightarrow R$, with $-r_A = 0.001 C_A C_R$ mol/liter \cdot s. We wish to process 1.5 liters/s of a $C_{A0} = 10$ mol/liter feed to the highest conversion possible in the reactor system consisting of four 100-liter mixed flow reactors connected as you wish and any feed arrangement. Sketch your recommended design and feed arrangement and determine C_{Af} from this system.
- 6.12.** A first-order liquid-phase reaction, 92% conversion, is taking place in a mixed flow reactor. It has been suggested that a fraction of the product stream, with no additional treatment, be recycled. If the feed rate remains unchanged, in what way would this affect conversion?
- 6.13.** 100 liters/hr of radioactive fluid having a half-life of 20 hr is to be treated by passing it through two ideal stirred tanks in series, $V = 40\,000$ liters each. In passing through this system, how much will the activity decay?
- 6.14.** At present the elementary liquid-phase reaction $A + B \rightarrow R + S$ takes place in a plug flow reactor using equimolar quantities of A and B. Conversion is 96%, $C_{A0} = C_{B0} = 1$ mol/liter. If a mixed flow reactor ten times as large as the plug flow reactor were hooked up in series with the existing unit, which unit should come first and by what fraction could production be increased for that setup?
- 6.15.** The kinetics of the aqueous-phase decomposition of A is investigated in two mixed flow reactors in series, the second having twice the volume of the first reactor. At steady state with a feed concentration of 1 mol A/liter and mean residence time of 96 sec in the first reactor, the concentration in the first reactor is 0.5 mol A/liter and in the second is 0.25 mol A/liter. Find the kinetic equation for the decomposition.
- 6.16.** Using a color indicator which shows when the concentration of A falls below 0.1 mol/liter, the following scheme is devised to explore the kinetics of the decomposition of A. A feed of 0.6 mol A/liter is introduced into the first of the two mixed flow reactors in series, each having a volume of 400 cm³. The color change occurs in the first reactor for a steady-state feed rate of 10 cm³/min, and in the second reactor for a steady-state feed rate of 50 cm³/min. Find the rate equation for the decomposition of A from this information.
- 6.17.** The elementary irreversible aqueous-phase reaction $A + B \rightarrow R + S$ is carried out isothermally as follows. Equal volumetric flow rates of two liquid streams are introduced into a 4-liter mixing tank. One stream contains 0.020 mol A/liter, the other 1.400 mol B/liter. The mixed stream is then

passed through a 16-liter plug flow reactor. We find that some R is formed in the mixing tank, its concentration being 0.002 mol/liter. Assuming that the mixing tank acts as a mixed flow reactor, find the concentration of R at the exit of the plug flow reactor as well as the fraction of initial A that has been converted in the system.

- 6.18.** At present conversion is $2/3$ for our elementary second-order liquid reaction $2A \rightarrow 2R$ when operating in an isothermal plug flow reactor with a recycle ratio of unity. What will be the conversion if the recycle stream is shut off?
- 6.19.** We wish to explore various reactor setups for the transformation of A into R. The feed contains 99% A, 1% R; the desired product is to consist of 10% A, 90% R. The transformation takes place by means of the elementary reaction



with rate constant $k = 1$ liter/mol \cdot min. The concentration of active materials is

$$C_{A0} + C_{R0} = C_A + C_R = C_0 = 1 \text{ mol/liter}$$

throughout.

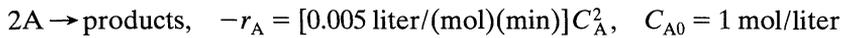
What reactor holding time will yield a product in which $C_R = 0.9$ mol/liter (a) in a plug flow reactor, (b) in a mixed flow reactor, and (c) in a minimum-size setup without recycle?

- 6.20.** Reactant A decomposes with stoichiometry $A \rightarrow R$ and with rate dependent only on C_A . The following data on this aqueous decomposition are obtained in a mixed flow reactor:

τ , sec	C_{A0}	C_A
14	200	100
25	190	90
29	180	80
30	170	70
29	160	60
27	150	50
24	140	40
19	130	30
15	120	20
12	110	10
20	101	1

Determine which setup, plug flow, mixed flow, or any two-reactor combination gives minimum τ for 90% conversion of a feed consisting of $C_{A0} = 100$. Also find this τ minimum. If a two-reactor scheme is found to be optimum, give C_A between stages and τ for each stage.

- 6.21.** For an irreversible first-order liquid-phase reaction ($C_{A0} = 10$ mol/liter) conversion is 90% in a plug flow reactor. If two-thirds of the stream leaving the reactor is recycled to the reactor entrance, and if the throughput to the whole reactor-recycle system is kept unchanged, what does this do to the concentration of reactant leaving the system?
- 6.22.** At room temperature the second-order irreversible liquid-phase reaction proceeds as follows:



A batch reactor takes 18 min to fill and empty. What percent conversion and reaction time should we use so as to maximize the daily output of product R?